

# PATENT ABSTRACTS OF JAPAN

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## (54) SECONDARY BATTERY

(57)Abstract:

PURPOSE: To improve the performance of a nonaqueous electrolyte secondary battery.  
CONSTITUTION: In a nonaqueous electrolyte secondary battery using a spinel lithium manganese composite oxide as the main active material in a positive electrode, to improve the cycle performance, a solid lithium-ion conductor is contained in a positive electrode as an ion conductor auxiliary agent to the main active material.  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  ( $0 < x \leq 1.0$ ,  $0 \leq y \leq 1$ ) known as a good lithium ion conductor is effective as the ion conductor auxiliary agent, and by mixing 5 molar% or more the lithium ion conductor based on the mole of the positive main active material to the positive electrode, the cycle performance is substantially improved. When a carbonaceous material is used in a negative electrode, the relation of the number of moles of manganese (a), the sum of the number of moles of cobalt and that of nickel (b), and the number of moles of carbon (c) contained in a negative active material layer facing to the positive electrode is set in the range of  $0.12 \leq (a+2b)/2c \leq 0.17$  to ensure the safety in overcharge.

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## CLAIMS

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[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by having blended the solid lithium ion conductor at the main active material, and making it contain in said positive electrode in the nonaqueous electrolyte rechargeable battery which is a cell which has a positive electrode, a negative electrode, SEBAPATA, and nonaqueous electrolyte, and uses a spinel mold lithium manganese multiple oxide for said positive electrode as a main active material.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 using the carbon material in which a dope and a dedope of a lithium are possible to a negative electrode as a main active material.

[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 using the lithium titanate-acid shown in a negative electrode by general formula  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  (however,  $0 \leq x \leq 1/3$ ) as a main active material.

[Claim 4]  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 < x < 1$ ,  $0 \leq y \leq 1$ ) is mixed less than [ more than 5 mol % 20 mol % ] to the positive-electrode main active material as a lithium ion conductor in the positive electrode. the mol of Mn contained in a positive-active-material layer -- the mol of a number (a), and Co and nickel -- the mol of the sum (b) of a number and a positive electrode, and the active material carbon contained in the negative-electrode active material layer which counters -- a number (c) The nonaqueous electrolyte rechargeable battery according to claim 2 characterized by having the relation of  $0.12 \leq (a+2b)/2c \leq 0.17$ .

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

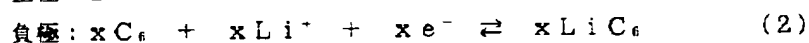
[0001]

[Industrial Application] This invention relates to the engine-performance improvement of a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] While miniaturization of electronic equipment and lightweight-ization are advanced, the request of the rechargeable battery of a high energy consistency has become strong further as the power source. In order to reply to the request, the nonaqueous electrolyte rechargeable battery attracted attention and the utilization has been tried. although the so-called lithium secondary battery which uses a lithium metal especially for a negative electrode was considered for possibility to be the largest, in order that the engine performance deteriorates remarkably, and it may BAUDA-ize by the repeat of charge and discharge, a metal lithium may deposit in a dendrite and a metal lithium negative electrode may cause internal short-circuit, a problem is in a practical cycle life and it is now -- utilization is difficult. So, recently, the nonaqueous electrolyte rechargeable battery which uses the carbon electrode using receipts and payments of the lithium ion to carbon as a negative electrode is developing.

This cell was named the rechargeable lithium-ion battery, was begun in 1990, was introduced to the world by this invention person etc., and by current, it is recognized, so that it is called a next-generation rechargeable battery "a rechargeable lithium-ion battery" also at the cell industry and a society (magazine Progress In Batteries & SolarCells, Vol. refer to 9, 1990, and p209), and it has required the spur for that utilization. A lithium content multiple oxide is typically used for a positive-electrode ingredient, and carbonaceous ingredients, such as corks and graphite, are used for a negative electrode. LiCoO<sub>2</sub> is used as a positive-electrode ingredient, a special carbon material (pseudo-graphite ingredient with a certain amount of random layer structure) is actually used for a negative electrode, and although a rechargeable lithium-ion battery with the energy density like 210 Wh/l is little, it is already used as a power source of a cellular phone or a video camera. However, as a big fault of this cell, it is that the price of a cell becomes high. One of them is to need a overcharge protection network. Since the rechargeable lithium-ion battery by which current utilization is carried out has the danger of igniting when it overcharges, it equipped with the overcharge protection network IC-ized in the cell pack, and it has been coped with. Moreover, it is the big factor to which it also becomes high [ a cell price ] to use expensive cobalt. Since it is scarce in resource, a price fall of cobalt cannot be desired in the future. When considering a cheap rechargeable lithium-ion battery, a lithium manganese multiple oxide is a very attractive positive-electrode ingredient. A lithium manganese multiple oxide (LiMn<sub>2</sub>O<sub>4</sub> grade) is a cheap ingredient, and in addition, its safety in overcharge is very high, and it does not need a overcharge protection network. The cell reaction of the rechargeable lithium-ion battery which used LiCoO<sub>2</sub> for positive active material, and used the carbonaceous ingredient for the negative electrode is as follows. At the charge-and-discharge reaction of normal



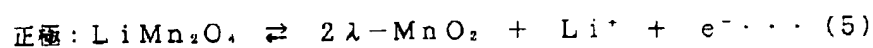
$$(x \approx 0.6)$$

It sets to overcharge

and is positive-electrode:  $\text{Li}_{1-x}\text{CoO}_2 \rightarrow \text{Li}_{1-x-\alpha}\text{CoO}_2 + \alpha\text{Li}^+ + \alpha e^- \quad (3)$

Negative electrode:  $\text{LiC}_6 + \alpha\text{Li}^+ + \alpha e^- \rightarrow \text{LiC}_6 + \text{Li}^0 \text{ (metal)} \quad (4)$

In charge of normal, about 60 percent of the lithium in positive active material is drawn out, and it is doped by the carbon in a negative electrode. And although positive active material serves as Li<sub>1-x</sub>CoO<sub>2</sub> (x\*0.6), the lithium which the further remaining lithium will be drawn out in overcharge and drawn out in overcharge deposits on a negative-electrode front face as a metal lithium in a negative electrode. Since the metal lithium which deposited on this negative-electrode front face is activity very much, there is about reacting violently with the electrolytic solution and carrying out a thermal run away, and anxiety is in the safety in overcharge. On the other hand, when a lithium manganese multiple oxide (LiMn<sub>2</sub>O<sub>4</sub> grade) is used for a positive electrode, the reaction (5) shown below at the charge-and-discharge reaction of normal is a positive-electrode reaction. That is, most lithiums in a positive electrode are drawn out in charge of normal, and the lithium which moves to a negative electrode from the inside of a positive electrode does not exist any longer in overcharge. Therefore, a metal lithium does not deposit in a negative electrode by overcharge, and the safety in overcharge is secured.



However, though regrettable, since the rechargeable lithium-ion battery which uses a lithium manganese multiple oxide as a positive-electrode ingredient has large degradation of the capacity accompanying a charge-and-discharge cycle and degradation of the capacity accompanying the charge-and-discharge cycle under an elevated temperature (35 degrees C or more) is especially large, having a price side and the big features in respect of safety, it is not put in practical use yet.

[0003]

[Problem(s) to be Solved by the Invention] A spinel mold lithium manganese multiple oxide is used as a main positive-active-material ingredient, the safety in overcharge is also high and, as for this invention, a cycle property also tends to offer a good rechargeable lithium-ion battery.

[0004]

[Means for Solving the Problem] It mixes with the lithium manganese multiple oxide which is main positive active material in a positive electrode, and a solid lithium ion conductor is made to contain. The one concrete approach at the time of using a carbon material as a negative-electrode active material Less than [ more than 5 mol %50 mol % ]  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$  the mol of Mn which mixes ( $0 \leq y \leq 1$  [ however, ]), creates a positive electrode, and is contained in a positive-active-material layer -- the mol of a number (a), and Co and nickel -- the mol of the sum (b) of a number, a positive electrode, and the active material carbon contained in the negative-electrode active material layer which counters -- between numbers (c) It is made to have the relation of  $0.12 \leq (a+2b)/2c \leq 0.17$ .

[0005]

[Function] The rechargeable lithium-ion battery which used the multiple oxide shown by general formula  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 \leq y \leq 1$ ) represented with  $\text{LiCoO}_2$  as positive active material shows a good charge-and-discharge cycle property. in this case, in charge (charge electrical-potential-difference 4.2V) of normal, about 60% of the lithium which existed in positive active material should lengthen, and blunder -- in positive active material, 40% of lithium remains also at the completion time of charge. Therefore, since the ionic conduction of an active material is kept good with enough residual lithiums in an active material, capacity degradation accompanying the cycle of charge and discharge is considered to be few things. However, the residual lithium in positive active material causes the metal lithium deposit to a negative electrode in overcharge, and spoils the safety in overcharge as stated above.

[0006] On the other hand, in the rechargeable lithium-ion battery which uses a spinel mold lithium manganese multiple oxide (typically  $\text{LiMn}_2\text{O}_4$ ) for positive active material, most lithiums in positive active material will be drawn out in the charge reaction (charge electrical-potential-difference 4.2V) of normal. This is a safe reason in overcharge, and, on the other hand, it is also considered the cause of capacity degradation accompanying the cycle of charge and discharge. That is, at the completion time of charge, there are very few residual lithiums in positive active material, the ionic conduction from which the migration in the active material crystal of a lithium ion should also be hung down is spoiled, and it is considered [ that the active materials which cannot react increase in number gradually or ] the cause of capacity degradation. In order for the charge-and-discharge reaction of an electrode active material to advance efficiently, the

good electronic conduction and the ionic conduction to all active materials must be maintained. Electronic conduction grant to an active material is performed by mixing of electric conduction assistants, such as graphite and acetylene black, from the former, and a precedent does not have \*\* about the ionic conduction grant to an active material.

[0007] In this invention, lithium ion conductivity tends to be given to the active material with which the residual lithium decreased also at the completion time of charge, and the conductivity of a lithium ion was spoiled by making the solid-state which has lithium ion conductivity in a positive electrode contain, and it is going to improve sharply the cycle property of the rechargeable lithium-ion battery which used the spinel mold lithium manganese multiple oxide as positive active material. It is known that  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 < x < 1$ ,  $0 \leq y \leq 1$ ) which drew out Li to some extent from  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$  is a good lithium ion conductor. Therefore, this invention can be carried out as one practice because you make it contain in a positive electrode by making  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 < x < 1$ ,  $0 \leq y \leq 1$ ) into an ionic conduction adjuvant.

[0008] What is necessary is to mix  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 \leq y \leq 1$ ) more than at 5 mol % to the lithium manganese multiple oxide which is the main active material in concrete operation, and just to create a positive electrode. added  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$  -- as an active material -- working -- a part -- a lithium ion should lengthen and blunder -- since it exists in a positive electrode in the state of  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 < x < 1$ ,  $0 \leq y \leq 1$ ), it works effectively as an ionic conduction adjuvant, and the charge-and-discharge effectiveness of the main active material is maintained good. However, mixing of  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$  will raise the positive-electrode cost of materials fundamentally, and Since the residual lithium in  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  also becomes the cause which causes a deposit of the metal lithium to a negative electrode in overcharge, and spoils the safety in overcharge this invention --  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  -- a positive-electrode main active material - - receiving -- less than [ more than 5 mol % 50 mol % ] -- desirable -- less than [ 30 mol % ] -- it regulates less than [ 20 mol % ] still more preferably. the mol of Mn contained in a positive-active-material layer when creating a cell as a negative-electrode active material furthermore using a carbonaceous ingredient -- the mol of a number (a), and Co and nickel -- the mol of the sum (b) of a number and a positive electrode, and the active material carbon contained in the negative-electrode active material layer which counters - - when a number (c) fills the relation of  $0.12 \leq (a+2b)/2c \leq 0.17$ , the safety in overcharge is also secured.

[0009] In the above-mentioned formula,  $(a+2b)/2$  are equal to the amount of lithiums (Z) originally contained in the negative electrode before first time charge, and the positive-active-material layer which counters. As a result of this invention person's changing the mixed ratio of a lithium manganese multiple oxide and  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$ , and the value of  $Z/c$  and carrying out comparison examination of the cell property, each of cell capacity, safeties in overcharge, and charge-and-discharge cycle engine performance found out said range secured enough.

[0010]

[Example] Hereafter, an example explains this invention in more detail.

[0011] The example of this invention to the cell which uses an example 1 carbonaceous ingredient as a negative-electrode active material is explained about a cylindrical cell, referring to drawing 1 -4. Drawing 1 shows the whole cell structure of this example. The cell component which is a generation-of-electrical-energy element for carrying out this

invention was prepared as follows. the N-methyl-2-pyrrolidone which the polyvinylidene fluoride (PVDF) 10 weight section is added to 86 weight sections of the meso carbon micro bead ( $d_{002}=3.37\text{\AA}$ ) which heat-treated at 2800 degrees C as 4 weight sections of aceti REMBU black, and a binder, and is a solvent, and wet blending -- carrying out -- a negative electrode -- a mixture -- it considered as the paste. and this negative electrode -- a mixture -- the paste was applied to homogeneity by various coverage to both sides of copper foil with a thickness of 0.01mm it is thin to a negative-electrode charge collector, pressurization molding was carried out with the roller press machine after desiccation, various active material carbon contents were made to contain, and the band-like negative electrode (1) was created.

[0012] Then, the positive electrode was prepared as follows. A commercial manganese dioxide ( $\text{MnO}_2$ ) and a commercial lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) were mixed so that the atomic ratio of Li and Mn might turn into a presentation ratio of 1:2, this was calcinated at 750 degrees C among air for 20 hours, and  $\text{LiMn}_2\text{O}_4$  was adjusted. Next, a commercial lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and cobalt carbonate ( $\text{CoCO}_3$ ) were mixed so that the atomic ratio of Li and Co might turn into a presentation ratio of 1:1, and it calcinated at 850 degrees C among air for about 5 hours, and  $\text{LiCoO}_2$  was adjusted. in this way, adjusted  $\text{LiMn}_2\text{O}_4$  -- the N-methyl-2-pyrrolidone which  $\text{O}_4$  and  $\text{LiCoO}_2$  are mixed by the various mole ratios shown in Table 1, and the acetylene black 2 weight section and the graphite 8 weight section may be added to the mixture 87 weight section, and it mixes, and are the polyvinylidene fluoride 3 weight section and a solvent as a binder further -- adding -- wet blending -- carrying out -- the mixing ratio of  $\text{LiCoO}_2$  to  $\text{LiMn}_2\text{O}_4$  -- the positive electrode with which rates differ -- a mixture -- the paste was prepared. this positive electrode -- a mixture -- it applied to homogeneity by various coverage to both sides of aluminium foil with a thickness of 0.02mm it is thin to a positive-electrode charge collector, and pressurization molding was carried out with the roller press machine after desiccation, and the paste made the various amounts of active materials contain, and created the band-like positive electrode (2).

[0013] In this way, the negative electrode (1) and positive electrode (2) which were created were wound up in the shape of a roll on both sides of the separator made from porosity polypropylene (3) in the meantime, and created the cell component as a winding object with an average outer diameter of 15.7mm. Next, an electric insulating plate (5) is installed in the pars basilaris ossis occipitalis of an iron cell can (4) which performed nickel plating, and the above-mentioned cell component is contained. The negative-electrode lead (6) taken out from the cell component is welded to the bottom of the above-mentioned cell can, and the mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) which dissolved one mol [1. ]  $\text{LiPF}_6$  into the cell can is poured in as the electrolytic solution. Then, an electric insulating plate (5) is installed also in the upper part of a cell component, a gasket (7) is inserted in, and an explosion-proof valve (8) is installed in the interior of a cell, as shown in drawing 1 . Before the positive-electrode lead (9) taken out from the cell component injects the electrolytic solution into this explosion-proof valve, it is welded. On the explosion-proof valve, the lock out lid (10) used as a positive-electrode external terminal was piled up on both sides of the doughnut mold PTC switch (11), the outer diameter of 16.5mm was created in total with the cell structure which shows the edge of a cell can in drawing 1 , and a total of 15 kinds of cells of cell (A) - (O) were created in height of 65mm. 15 kinds of this cell serves as a design

value shown in Table 1, respectively.

[0014] After making it pass the aging period of 12 hours in ordinary temperature for the purpose of the stabilization inside a cell, each created cell set the charge upper limit electrical potential difference as 4.2V, performed charge of 8 hours in ordinary temperature, similarly performed discharge to termination electrical-potential-difference 3.0V by 800mA constant-current discharge about all cells in ordinary temperature, and calculated the initial discharge capacity of each cell. Initial discharge capacity is shown in Table 2.

表 1

試作電池	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
正極中 LiCoO <sub>2</sub> 混合モル%	0	3.0	5.0	100	10	20	50	10	20	50	20	50	20	50	20
$\frac{Z}{c}$	0.148			0.125			0.112			0.166			0.179		0.19

ただし表中の Z : 負極と対向する正極活物質層に元来含有していたリチウム量。

c : 正極と対向する負極活物質層に含有する活物質炭素のモル数。

表 2

試作電池	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
初期放電 容量 (Ah)	1.09	1.08	1.07	0.82	0.97	0.94	0.85	0.91	0.88	0.79	1.09	1.00	1.13	1.04	1.13

Each cell performed the charge-and-discharge cycle trial at 40 degrees C after that. The charging current is 400mA, and the charge upper limit electrical potential difference was set as 4.2V, charge of 4 hours was performed, and discharge went by 800mA constant-current discharge to termination electrical-potential-difference 3.0V, and repeated charge and discharge.

[0015] To the cell (D) by which the cycle property used LiCoO<sub>2</sub> 100% as shown in drawing 2 being 85% or more of high capacity maintenance factor also after 150 cycles, the capacity fall accompanying a cycle is large and the cell (A) which has not added LiCoO<sub>2</sub> at all will fall to about the one half of initial capacity like 150 cycles. however, by the cell which mixed 5% or more of LiCoO<sub>2</sub>, a capacity maintenance factor is improved for the cell (D) and \*\* which used LiCoO<sub>2</sub> 100% by whenever. However, mixing of three-mol % of LiCoO<sub>2</sub> is inadequate, and it turns out at least that the effective improvement of a capacity maintenance factor needs [ 5% or more of LiCoO<sub>2</sub> ] to be mixed. If the relation between the initial discharge capacity of each cell and the mixed ratio of LiCoO<sub>2</sub> to each cell is furthermore looked at based on the result of Table 2 If it



increases in the mixed ratio of  $\text{LiCoO}_2$  when  $Z/c$  is fixed as shown in drawing 3, it will decrease in capacity. Since one is in the point which is an ingredient with the cheap big features of the rechargeable lithium-ion battery which uses a lithium manganese multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) as a positive-electrode ingredient, addition of expensive  $\text{LiCoO}_2$  is and still more preferably [ 20% or less of ] desirable 30% or less preferably 50% or less. Furthermore, since initial capacity all becomes small when  $Z/c$  is 0.112 (cells H, I, and J),  $0.12 \leq Z/c$  is required.

[0016] Another big features of the rechargeable lithium-ion battery which uses a lithium manganese multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) as a positive-electrode ingredient are in the safety in overcharge. The cell made as an experiment evaluated the safety in overcharge as follows. First, as charge of normal, the charging current was 400mA, and the charge upper limit electrical potential difference was set as 4.2V, and performed charge of 4 hours. Then, the charge upper limit electrical potential difference was set as 10V, the charging current was raised to 1.6A, overcharge was performed for 1 hour, the highest attainment temperature on the front face of a cell was measured, and it was shown in drawing 4. By 0.17 or less cell, although about 120 degrees C was the highest attainment temperature, the cell of  $Z/c=0.19$  blew off fire from the interior of a cell after all by having gone up to 160 degrees C or more by  $Z/c=0.179$ , and  $Z/c$  has reached the temperature of 300 degrees C or more. Previously although [ from a viewpoint of cell capacity ] it is  $0.12 \leq Z/c$ , from the point of the safety of overcharge, it should consider as  $Z/c \leq 1.7$ . The value of  $Z$  used here is the amount of lithiums ( $Z$ ) originally contained in the negative electrode before first time charge, and the positive-active-material layer which counters. relation with the amount of transition elements (an example Mn and Co) in positive active material -- setting --  $Z = (a+2b)/2$  (however, a --)  $b$  is the number of content mols of Mn and Co in a positive electrode, respectively, and according to any charge-and-discharge conditions, since  $(a+2b)/2$  are eternal, they can be expressed as follows as optimal design value which can secure the safety of overcharge with this for convenience.

$0.12 \leq (a+2b)/2c \leq 1.7$  [0017] The lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), cobalt carbonate ( $\text{CoCO}_3$ ), and nickel carbonate ( $\text{NiCO}_3$ ) of example 2 marketing were mixed so that Li and the atomic ratio of Co and nickel might turn into a presentation ratio of 1:0.5:0.5, and it calcinated at 850 degrees C among air for about 5 hours, and the lithium cobalt nickel multiple oxide ( $\text{LiCo}_0.5\text{nickel}_0.5\text{O}_2$ ) was adjusted. It mixed by the mole ratio shown in Table 3 at  $\text{LiMn}_2\text{O}_4$  adjusted in the example 1, and adjusted  $\text{LiCo}_0.5\text{nickel}_0.5\text{O}_2$  created a cell (P), (Q), and (R) completely like the example 1 by having used the mixture as positive active material, performed the same evaluation as an example 1, and showed the result in Table 3. In the example 2,  $\text{LiCo}_0.5\text{nickel}_0.5\text{O}_2$  was used instead of  $\text{LiCoO}_2$  in an example 1, and a cell (P) is the proper design value found out in the example 1, and the cell (Q) serves as design value shifted from the proper range by  $Z/c=0.19$ , and made the cell (R) as an experiment in the range where the amount of mixing of  $\text{LiCo}_0.5\text{nickel}_0.5\text{O}_2$  is inadequate.

[0018] For a cell (P), to the satisfactory result predicted [ in / as the result was shown in Table 3 / capacity, the safety in overcharge, and all cycle properties ] from the result of an example 1 having been shown, the safety in overcharge is not secured but a cell (R) is [ a cell (Q) ] a cycle property small.

表 3

試作電池	P	Q	R
正極中 $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ 含有モル%	20	20	3.0
$\frac{Z}{c}$	0.14	0.19	0.14
初期容量 (mAh)	1000	1162	1057
過充電での安全性 (最高到達温度)	120℃	発火	120℃
100サイクル までの容量維持率 (%)	91	—	75

property smell.

It turns out that a large result of \*\*\*\*\* degradation is brought, and the same result is obtained even if it uses  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  instead of  $\text{LiCoO}_2$ . Therefore, in the rechargeable lithium-ion battery which uses a lithium manganese multiple oxide as positive active material, it is clear that it is effective in an improvement of the cycle property to make  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 < x < 1$ ,  $0 \leq y \leq 1$ ) known as a good ion conductor of a lithium ion contain as an ionic conduction adjuvant in a positive electrode. [0019] Moreover, naturally the cycle property improvement technique of adding ionic conduction to this spinel mold lithium manganese multiple oxide can also use other lithium ion conductors as an ionic conduction adjuvant.

[0020] Although the meso carbon micro bead ( $d_{002}=3.37\text{\AA}$ ) which heat-treated at 2800 degrees C as a negative-electrode active material was used in the above-mentioned example, the same effectiveness can be expected also when using other carbon materials (pitch coke, petroleum system corks, natural graphite, etc.) as a negative-electrode active material.

[0021] Furthermore, the first improvement by this invention sets a spinel mold lithium manganese multiple oxide to the nonaqueous electrolyte rechargeable battery used as positive active material. It is what adds ionic conduction to positive active material, and improves a cycle property. The first improvement by this this invention other than a carbon material For example, a lithium metal and a lithium alloy, Sulfide of transition metals ( $\text{TiS}_2$ ,  $\text{NbS}_2$ ,  $\text{VS}_2$  grade) It can apply, also when using  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  ( $0 \leq x \leq 1/3$ ) and  $\text{Nb}_2\text{O}_3$  grade as a negative-electrode active material.

[0022] Moreover, although the mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) which dissolved one mol [1. ]  $\text{LiPF}_6$  in the negative-electrode active material used by this example as one of the electrolytic solutions which suit best was used in this example, the nonaqueous electrolyte constituted by dissolving can use various kinds of lithium salt for various kinds of non-aqueous solvents known from the former, choosing it as them from compatibility with the negative-electrode active material to be used. As a non-aqueous solvent which can constitute nonaqueous electrolyte, propylene carbonate, ethylene carbonate, gamma-butyrolactone,

dimethoxyethane, diethoxy ethane, diethylether, a tetrahydrofuran, dioxolane, a sulfolane, a methyl sulfolane, etc. are well-known, and they are used by independent [ these ] or two sorts or more, mixing. As lithium salt, they are  $\text{LiAsF}_6$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ , and  $\text{LiCF}_3\text{CO}_2$ .  $\text{LiCF}_3\text{SO}_3$  grade can be used.

[0023] The example which used the spinel system lithium titanate-acid ghost is shown in an example 3 negative-electrode active material.

The creation spinel system lithium titanate-acid ghost of a negative electrode exists in  $0 \leq x \leq 1/3$  in general formula  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ . At this example, it carries out by  $x=1/3$ . A lithium hydroxide ( $\text{LiOH}$ ) is often mixed with a titanium dioxide ( $\text{TiO}_2$ : anatase) by the 5/3 mol : 4/3 mol ratio, pressurization molding of the mixture is carried out at a pellet type, this is calcinated at 800 degrees C by the helium ambient atmosphere for 24 hours,  $\text{Li}_4 / 3\text{Ti}_5 / 3\text{O}_4$  is compounded and ground, and it adjusts to powder with a mean particle diameter of 10.5 microns. As 3 weight sections, the graphite 4 weight section, and the binder of carbon black, with the polyvinylidene fluoride 3 weight section, wet blending of the 90 weight sections of the adjusted lithium titanate-acid ghost ( $\text{Li}_4 / 3\text{Ti}_5 / 3\text{O}_4$ ) is carried out to the N-methyl-2-pyrrolidone which is a solvent, and they are made into a slurry (the shape of a paste). It applies to homogeneity to both sides of aluminium foil with a thickness of 0.02mm which uses this slurry as a charge collector, pressurization molding is carried out with the roller press machine after desiccation, and a band-like negative electrode (1b) is created.

[0024] It mixes by the mole ratio of 20:80 to  $\text{LiMn}_2\text{O}_4$  which adjusted  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  adjusted in the creation example 2 of a positive electrode in the example 1, and a positive electrode (2b) is created completely like an example 1 by using the mixture as positive active material.

[0025] The negative electrode (1b) and positive electrode (2b) of a cell which carried out creation \*\*\*\* and which were created are wound up in the shape of a roll on both sides of a separator (3) in the meantime, and create a cell component as a winding object with an average outer diameter of 15.7mm. in addition, the thing which sufficient reinforcement is held, the thinnest possible thing is desirable, and the separator of the porous product made from polypropylene or the product made from polyethylene is available as a commercial item, and was used in the example 1 here although the nonwoven fabric and porous membrane of the stable quality of the material could be used for the separator to the electrolytic solution -- the same -- the separator made from porosity polypropylene with a thickness of 0.025mm was used. Pouring in the mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) which dedicated the cell component to the cell can (4), and dissolved one mol [ /l. ]  $\text{LiClO}_4$  as the electrolytic solution, the rest completely created the cell (S) with an outer diameter [ of 16.5mm ], and a height of 65mm with the cell structure shown in drawing 1 as well as an example 1.

[0026] In the example positive-electrode creation of a comparison, except [ all ] having used as positive active material  $2\text{OLiMn}_4$  independent one adjusted in the example 1, it was the same as the example 3, and the cell (T) was created.

[0027] The cell (S) created in the example 3 and the example of a comparison and (T) After making the aging period of 12 hours pass in ordinary temperature for the purpose of the stabilization inside a cell, When the charge upper limit electrical potential difference was set as 3.2V, charge of 8 hours was performed in ordinary temperature and 800mA constant-current discharge similarly performed discharge to termination electrical-

potential-difference 2.0V in ordinary temperature, both a cell (S) and (T) showed the initial discharge capacity of 1000mAh(s). However, in the charge-and-discharge cycle trial in 40 degrees C of after that, the cell (T) which used 2OLiMn4 independent one as positive active material had the large capacity fall accompanying a cycle, and it fell to about the one half of initial capacity like 150 cycle. On the other hand, the cell (S) was 85% or more of high capacity maintenance factor also after 150 cycles. Moreover, also in the overcharge trial, the cell (S) stopped at 120 degrees C or less, and the attainment maximum temperature of it was a safe result.

[0028]

[Effect of the Invention] as mentioned above, if  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 \leq y \leq 1$ ) is mixed more than at 5 mol % to the lithium manganese multiple oxide which is the main active material and a cell is created, added  $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$  should work also as an active material, and a part of lithium ion should lengthen it, and it should blunder -- in a positive electrode, it exists in the state of  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  (however,  $0 < x < 1$ ). Since  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  ( $0 < x < 1$ ,  $0 \leq y \leq 1$ ) is a good ion conductor, it works effectively as an ionic conduction adjuvant, and it serves as a rechargeable lithium-ion battery with little capacity degradation accompanying a charge-and-discharge cycle. however -- since the residual lithium in  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  also becomes the cause which causes a deposit of the metal lithium to a negative electrode in overcharge, and spoils the safety in overcharge -- this invention --  $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$  -- a positive-electrode main active material -- receiving -- less than [ 50 mol % ] -- desirable -- less than [ 30 mol % ] -- it regulates less than [ 20 mol % ] still more preferably. the mol of Mn contained in a positive-active-material layer when using a carbon material especially for a negative electrode as an active material -- the mol of a number (a), and Co and nickel -- the mol of the sum (b) of a number and a positive electrode, and the active material carbon contained in the negative-electrode active material layer which counters -- when a number (c) fills the relation of  $0.12 \leq (a+2b)/2c \leq 0.17$ , the safety in overcharge is secured. According to this invention, the high capacity and the long lasting and safe rechargeable lithium-ion battery which a cheap lithium manganese multiple oxide can use now as a positive-electrode main active material of a rechargeable lithium-ion battery, and can fully replace also with the existing rechargeable battery can provide now cheaply, and the industrial value is size.

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